PB86-191400

Nature of Organics Removed during Treatment of Mississippi River Water

Minnesota Univ., Minneapolis

Prepared for

Environmental Protection Agency, Cincinnati, OH

Feb 86

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. R PB86-191400
EPA/600/J-86/026		

4. TITLE AND SUBTITLE	5. REPORT DATE
THE NATURE OF ORGANICS REMOVED DURING TREATMENT OF MISSISSIPPI RIVER WATER (Journal Version)	1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) M.J. Semmens[1] and A.B. Staples[2]	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS [1]University of Minnesota, Minneapolis, MN 55455-0220 [2]3M Co., St. Paul, MN 55144	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. CR 806377 byproduct
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory-Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED Journal Article
	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer, A. Stevens, 513-569-7342
J. American Water Works Association, 78(2):76-81, Feb. 1986

16. ABSTRACT

In light of increasing concern for the organic content of potable water supplies and the production of potentially toxic chlorinated organic products, a better understanding of the character of organics removed by commonly used treatment processes is desirable. A variety of chemical and physical characterization techniques were used to identify the changes in organic character resulting from chemical treatments of a Mississippi River water sample.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	8
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA/600/J-86/026
JOURNAL ARTICLE

The Nature of Organics Removed During Treatment of Mississippi River Water

M.J. Semmens and A.B. Staples

In light of increasing concern for the organic content of potable water supplies and the production of potentially toxic chlorinated organic products, a better understanding of the character of organics removed by commonly used treatment processes is desirable. A variety of chemical and physical characterization techniques were used to identify the changes in organic character resulting from chemical treatments of a Mississippi River water sample.

Water treatment facilities across the United States employ a variety of treatment processes for the production of potable water. The choice of process is determined by the quality of the source water and the local treatment objectives. Lime softening is widely employed where hardness must be reduced to an acceptable level. This process can also be successfully operated for the simultaneous reduction of color as in Minneapolis-St. Paul, Minn. A recent study[1] examined the effect of conditions such as pH, initial hardness, and lime dose on the removal of natural organic matter during chemical softening of Mississippi River water. Coagulation is also widely employed for the reduction of turbidity or color in waters with an acceptable hardness level, and numerous studies have documented the performance of this process for removing organics.[2]

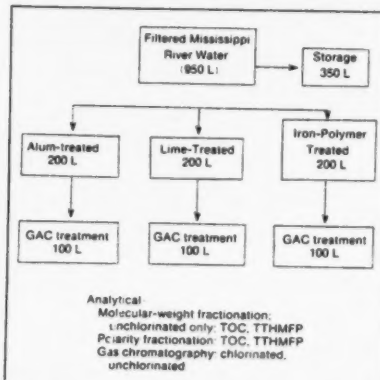

Figure 1. Sampling and analysis schematic for organic characterization studies

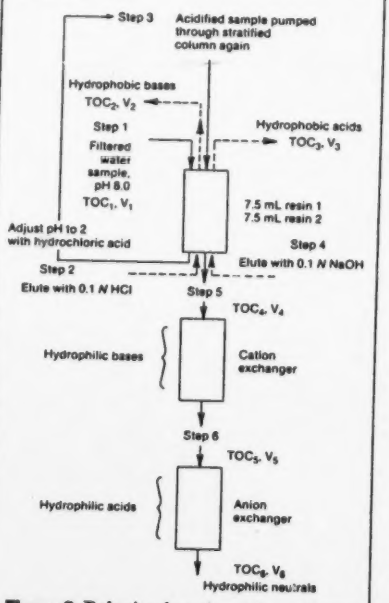

Figure 2. Polarity fractionation scheme (*after Leenheer*[6])

Experimental methods

A 950-L sample of Mississippi River water was collected close to the extraction point of a Mississippi treatment plant. The sample was split into three fractions, pretreated by alum coagulation, lime softening, and ferric-sulfate-polymer coagulation, respectively. Samples of the pretreated waters were further treated by activated carbon. Figure 1 shows the overall treatment scheme.

Treatment methods. Treatment studies were conducted on the river water to evaluate the dose-response behavior of the sample and to identify the chemical doses that should be used. The selected conditions are summarized in Table 1. The coagulant doses gave comparable organics removals of approximately 60-70 percent (ultraviolet absorbance), and little benefit was observed with larger coagulant doses. The choice of polymer was based on extensive jar-test evaluations of numerous polymers.[1] The selected lime dose was also determined from a softening study and was sufficient to achieve a desired residual hardness of 80 mg as $CaCO_3$/L. The lime-treated water was recarbonated by sodium bicarbonate addition and a small amount of sulfuric acid to reduce the final pH to 9.0.

Pretreatment-coagulation. River water samples (100 L) were transferred to a 160-L stainless steel tank. The contents of the tank were rapid mixed by a 0.3-hp (200-W) direct-drive motor coupled to a stainless steel impeller. Coagulant was added and rapid mixing was continued for 10 s. Slow mixing was done for 30 min by three stainless steel paddles driven by a 0.15-hp (100-W) high-speed motor fitted with a 20:1 reduction gear. The rotational speed was controlled between 10 and 30 rpm by a variable transformer. The stainless steel stirrer was insulated from the drive motor by tapping a 15-mm plexiglass rod into the drive shaft. This prevented electrical interference from the motor affecting the measurement of solution pH. The pH of the sample was adjusted immediately after rapid mixing.

After flocculation, the contents of the tank were allowed to settle for 1 h. The supernatant was then pumped at a flow rate of 250 mL/min through a trimedia filter. The filter was housed in a 100-mm-diameter glass column and consisted of 23 cm each of anthracite, sand, and garnet. Filtrate was stored in covered 40-L stainless steel tanks.

Pretreatment. The procedure for lime softening was similar except that rapid mixing was extended to 30 s and good clarification usually required more than 1 h of sedimentation. The initial hardness of the river water was 188 mg as $CaCO_3$/L of which 45 mg/L was magnesium. The pH rose to between 10.7 and 10.9 during the softening process. After recarbonation, total hardness was reduced to 80 mg/L. Following these pretreatments, the water was filtered through a trimedia filter. The resulting water quality of the treated samples is presented in Table 2.

Carbon treatment. Filtered water samples were pumped to minicolumns of granular activated carbon (GAC)* containing 50 × 80 carbon† supported on 2 cm of sand. The carbon was backwashed with carbon-filtered distilled water to remove fines and stratify the bed prior to use. The pretreated water samples were pumped through the carbon columns at

*Glenco 3400 Series, Spectrum Scientific Inc., Houston, Texas
†Nuchar WV-G, Westvaco Inc., Covington, Va.

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

3-4 mL/min (Table 3). The columns were sized to provide an average effluent TOC of about 1 mg/L, which necessitated the use of larger carbon depths for the softened water compared with the depths required for the iron-and alum-treated waters. The entire effluent volume from each column was collected, mixed, and stored for analysis. The organic content of the carbon-treated samples represents the average composition obtained from the columns over 10 to 12 days of operation, during which TOC breakthrough rose from 10 to 35 percent.

TABLE 1
Conditions of pretreatment

Alum coagulation
$Al_2(SO_4)_3 \cdot 18H_2O$*
Dose = 80 mg/L
pH = 5.0
Iron-polymer coagulation
$Fe_2(SO_4)_3 \cdot H_2O$†
Dose = 20 mg/L
Polymer‡
Dose = 3 mg/L
pH = 5.0
Lime softening
High calcium quicklime (CaO)§
Dose = 233 mg/L added as dry powder
Recarbonation $NaHCO_3$*

*Fischer Chemical, Philadelphia, Pa.
†Mallinckrodt Chemical, St. Louis, Mo.
‡Arco Performance Chemicals, Philadelphia, Pa.
§Sigma Chemical, St. Louis, Mo.

TABLE 2
Water quality after large-scale pretreatment

Pretreatment	TOC		UVA	
	mg/L	Removal *percent*	Absolute	Removal *percent*
None	6.3		0.840	
Alum	2.86	52	0.247	71
Iron-polymer	3.27	47	0.29	65
Lime-recarbonation	4.21	33	0.406	52

TABLE 3
Activated-carbon treatment conditions

Pretreatment	Volume Treated per Column *L*	Carbon Depth *cm*	EBCT* *min*	Flowrate *mL/min*	Composite Effluent TOC *mg/L*
Alum	50	11.7	2.2	3.5	0.98
Iron-polymer	50	14.4	2.7	3.35	1.06
Lime-recarbonation	50	24.1	4.5	3.5	1.17

*EBCT—empty bed contact time

Analytical methods

The techniques used in this study are described in detail elsewhere.[1,3] Total organic carbon (TOC) measurements were made using an organic analyzer,* which had an accuracy of ±5 percent above 1 mg/L TOC; below 1 mg/L, accuracy was ± 10 percent or 20 μg/L.

Ultraviolet absorbance (UVA) was measured on a spectrophotometer† using a 5-cm path length at 254 nm. All samples for TOC and UVA analysis were first adjusted to pH 4.0. Trihalomethane formation potential (THMFP) was measured according to a technique described elsewhere.[4] Molecular-weight fractionation was achieved using ultrafiltration membranes‡ according to a technique described elsewhere.[4]

A polarity fractionation scheme[5] was used to fractionate the organics according to their sorptive behavior on different resins.

Hydrophobic and hydrophilic organics were separated on a stratified column containing 8.5 g of resin 1§ on top of 8.5 g of resin 2,** following the procedure outlined in Figure 2. The hydrophilic organics were then separated into basic, acidic, and neutral fractions by passing the water through columns containing 8.5 g of cationic and anionic resins.†† Because of the low TOC of the waters tested, 15-L treated water samples and 5-L river water samples were fractionated. The corresponding capacity factors for $k'_{0.5r}$[7] were 750 for treated water and 250 for river water samples. The fractions are operationally defined by the conditions maintained during the fractionation procedure, but the terminology used in this article is the same as that employed by Leenheer and Huffmann.[5] Computation of the polarity fractions is documented in Table 4.

Results

Polarity fractionation. Hydrophobic organics, defined as those organics absorbed by the resins under the test conditions, were separated into basic, acidic, and neutral fractions. The hydrophilic organics were fractionated on the ion exchange resins, but the exchange capacities of the resins were exceeded, and the data obtained were unreliable. It was not possible to distinguish between hydrophilic neutrals and hydrophilic acids accurately. The hydrophilic base fraction was always small; therefore, the acid and neutral fractions are jointly referred to as the hydrophilic organic fraction. When the base fraction was included, the sum is referred to as the total hydrophilic organics fraction.

The results are summarized in Tables 5 through 8. The fractionation of the river water sample indicated that 40 percent of the organics content was characterized as hydrophobic and 60 percent as hydrophilic. The acidic and neutral fractions accounted for 93 percent of the total TOC. The hydrophobic organics were predominantly acidic (63 percent) in character, although a significant fraction (35 percent) of these organics were neutral (Table 5).

Treatment of the river water sample by either lime softening or coagulation reduced the concentrations of the acidic and neutral organic fractions and removed all the hydrophilic base fraction. Lime gave the poorest removals and appeared to be ineffective, at the applied dose, in removing the acidic fractions of both the hydrophilic and hydrophobic organics. (This was the only conclusive data collected on hydrophilic acids.) Furthermore, the data indicated an anomalous increase in the hydrophobic base fraction following lime treatment.

Granular activated carbon column treatment of the pretreated waters produced effluents that were essentially identical in quality and character. Regardless of the water pretreatment conditions, analysis of the carbon column effluent indicated that 70–80 percent of the organic compounds passing through the carbon were neutral in character and predominantly hydrophilic.

The treatment objective in the design of the carbon column study should be considered when comparing these data. The lime-pretreated water, with its higher TOC, required almost twice the depth of carbon to achieve the same desired average effluent concentration (~1 mg TOC/L).

*Barnsted Co., Boston, Mass.
†Model 26, Beckman Instruments, Fullerton, Calif.
‡Millipore Corp., Bedford, Mass.
§XAD8, Sigma Chemical Co., St. Louis, Mo.
**XAD2, Sigma Chemical Co., St. Louis, Mo.
††BioRad Laboratories, Richmond, Calif.

The fractionated samples of water were also analyzed for trihalomethane (THM) precursors. The NaOH and H_2SO_4 eluates were diluted* back to their equivalent river water volume. The dilution ratio was equal to the volume of river water treated in the resin column divided by the volume of eluate collected. Analyses conducted on the various water samples and their fractions are shown in Tables 7 and 8.

Analysis of the data contained in these tables indicates that the THM precursors in the raw river water were almost evenly split between the hydrophobic and hydrophilic fractions (47 versus 53 percent). In addition, acidic and neutral fractions of the sample accounted for the majority of the organic content, whereas the organic base fraction contributed a negligible amount. The negative numbers in Table 7 were caused by the computation technique employed and also, perhaps, by the fractionation scheme itself. For example, hydrophobic neutrals were calculated by subtracting three THM measurements from the THM concentration of the initial water sample. The accuracy of the hydrophobic neutral fraction is therefore the poorest of those reported. All other fractions were measured directly or by the subtraction of only two THM values. Negative values obtained for hydrophilic acidic and base fractions resulted from a situation in which the ion exchange column effluents were higher in THM precursors than their respective feeds. This problem was consistent enough, especially for the cation exchange column (hydrophilic bases), that it cannot simply be dismissed as experimental error. It is likely that the use of an acid form cation exchange resin may slightly alter the nature of the organic content, making it more susceptible to THM production. The effect is very slight, but the extremely low internal pH of the cation exchanger and the elevated internal ionic strength may encourage hydrolysis or alter the configuration of the polymeric humic macromolecules in such a way that THM production increases. The effect was relatively minor, and since little TOC was measured in the hydrophilic base fraction, the negative results were interpreted as being equivalent to zero THM production for this fraction. However, this effect caused a corresponding increase in the concentration of hydrophilic neutral precursors.

Pretreatment caused an approximately 70-percent decrease in THM precursors in the hydrophobic fraction and a 40–50 percent decrease in hydrophilic precursors. As shown in Table 8, the selective removal of hydrophobic THM precursors caused a significant increase in the ratio of hydrophilic to hydrophobic precursors.

The total THM precursor concentrations in the pretreated samples were

TABLE 4
Computation of polarity fractions

Hydrophobic bases	$H_B = V_2 \cdot TOC_2$
Hydrophobic acids	$H_A = V_3 \cdot TOC_3$
Hydrophobic neutrals	$= V_1 \cdot TOC_1 - H_A - H_B$
Hydrophilic bases	$= V_4 \cdot TOC_4 - V_5 \cdot TOC_5$
Hydrophilic acids	$= V_5 \cdot TOC_5 - V_6 \cdot TOC_6$
Hydrophilic neutrals	$= V_6 \cdot TOC_6$

TABLE 5
Polarity fractionation study TOC values

Treatment Description	Whole Sample	Polarity Fraction—*mg TOC/L*				
		Hydrophobic		Hydrophilic		
		Base	Acid	Neutral	Base	Acid + Neutral
None	6.27	0.05	1.57	0.87	0.36	3.42
Lime	4.21	0.18	1.06	0.32	0.00	2.65
Iron-polymer	3.27	0.05	0.71	0.36	0.08	2.07
Alum	2.86	0.05	0.71	0.20	0.10	1.87
Lime + GAC EBCT* = 4.5 min	0.95	0.01	0.06	0.12	0.03	0.73
Iron-polymer + GAC EBCT = 2.7 min	0.90	0.01	0.05	0.09	0.10	0.65
Alum + GAC EBCT = 2.2 min	0.92	0.01	0.04	0.14	0.10	0.63

*EBCT—empty bed contact time

TABLE 6
Fractionation study TOC values: comparison of hydrophobic and hydrophilic fractions

Treatment Description	Polarity Fraction—*mg TOC/L*		
	Hydrophobic	Hydrophilic	Ratio*
None	2.49	3.78	1.52
Lime	1.56	2.65	1.70
Iron-polymer	1.12	2.15	1.92
Alum	0.96	1.97	2.05
Lime + GAC EBCT = 4.5 min	0.19	0.76	4.00
Iron-polymer + GAC EBCT = 2.7 min	0.15	0.75	5.00
Alum + GAC EBCT = 2.2 min	0.19	0.64	3.37

*Ratio = hydrophilic fraction/hydrophobic fraction

TABLE 7
Polarity fractionation study TTHMFP values

Treatment Description	Whole Sample	Polarity Fraction—*mg THMFP/L*				
		Hydrophobic		Hydrophilic		
		Base	Acid	Neutral	Base	Acid + Neutral
None	456	3	119	84	-13	263
Lime	211	0	37	17	12	145
Iron-polymer	193	4	57	-4	-7	143
Alum	189	8	63	-2	-13	133
Lime + GAC EBCT = 4.5 min	47	0	0	25	-15	37
Iron-polymer + GAC EBCT = 2.7 min	31	8	4	-11	-6	36
Alum + GAC EBCT = 2.2 min	30	0	0	-5	-3	38

TABLE 8
Polarity fractionation study TTHMFP values: comparison of hydrophobic and hydrophilic fractions

Treatment Description	Polarity Fraction—*mg TTHMFP/L*		
	Hydrophobic	Hydrophilic	Ratio*
None	206	250	1.21
Lime	54	157	2.91
Iron-polymer	57	136	2.52
Alum	69	120	1.74
Lime + GAC EBCT = 4.5 min	25	22	0.88
Iron-polymer + GAC EBCT = 2.7 min	1	30	30.00
Alum + GAC EBCT = 2.2 min	-5	35	40.00

*Ratio = hydrophilic fraction/hydrophobic fraction

similar, ranging between 189 and 211 μg/L. The sum of the THM precursors in the sample fractions ranged between only 204 and 211 μg/L. The overall mass balance was, therefore, excellent.

The iron-polymer-treated and alum-treated waters were essentially identical in character and generated approximately equal THM concentrations in each fraction. The lime-treated water, however, showed a marked difference in character and THM precursor distribution. Trihalomethane precursors in the lime-pretreated water were found in the hydrophobic neutral fractions and the hydrophilic base fractions in higher concentratons than in the coagulated water. This was compensated for by a lower hydrophobic acid fraction, and the total THM production was roughly the same as for other pretreated waters.

The analysis of the samples treated by GAC revealed that the lime-pretreated water yielded the highest THM concentration after chlorination. Results of the fractionation analysis on this sample showed a significant precursor concentration attributable to the hydrophobic neutral fraction. It appeared that the hydrophobic neutral precursors were not effectively removed by activated carbon. In general, however, the 75–84 percent removals of the THM precursors achieved during carbon treatment of the different water samples may be accounted for by the removal of hydrophobic acids and hydrophilic organics.

Molecular-weight fractionation

The results of the molecular-weight fractionation studies are presented in Table 9. The river-water sample analysis revealed that 50 percent of the TOC was in the 1–10K fraction and 23 percent was less than 1K in size. The 10–100K and ≥100K fractions accounted for only 10 percent and 17 percent, respectively.

Analysis of the data in Table 9 indicates that all pretreatments removed the 10–100K TOC fraction. The effective difference between the pretreatments was apparent from their impact on the measured TOCs in the lower-molecular-weight fractions. Lime, iron-polymer, and alum treatments reduced the TOC content of the 1–10K fraction by 52 percent, 57 percent, and 68 percent, respectively. The coagulants did not cause any reduction in the fraction having a molecular weight less than 1000 nominal molecular weight (nmw) (1K). The lime-pretreated water, however, actually caused a 40-percent increase in the low-molecular-weight (≤1K) fraction. This can be explained if the lime treatment caused hydrolysis and a breakdown of the organic content in the higher-molecular-weight fractions.

For the activated carbon effluents, the distribution of TOC among the molecular-weight fractions was essentially constant. Approximately 70 percent of the effluent TOC was attributable to the ≤1K fraction, and approximately 25 percent was associated with the ≥100K fractions. The measured molecular-weight distribution of the river water agrees with the observations of earlier investigators. Eisenreich et al[8] measured the molecular-weight distribution of dissolved organic carbon in a Mississippi River water sample drawn at St. Anthony Falls, the same location employed in this study. Using a similar membrane separation technique, they found that the distribution of TOC gave 70 percent less than 10K, 15 percent in the range 10–25K, 12 percent in the 25–100K range, and 2 percent greater than 100K.

The molecular-weight distribution of the water was influenced significantly by coagulation with alum and iron. The higher-molecular-weight organics were more effectively removed by these hydrolyzing metal salts. This was anticipated since many previous studies provide evidence of this effect. For example, most of the organic color in surface waters is typically associated with the higher-molecular-weight humic acids,[9] and color may be removed effectively by coagulation.[2,10-13] In addition, higher-molecular-weight organic compounds in water are very large in size, and their polyelectrolyte character, provided by dissociated surface carboxyllic, phenolic, and ketonic functional groups, allows them to be classified as colloidal particles.[14] The separation of colloidal particles from water is the primary function of coagulation as it is practiced in conventional treatment facilities for turbidity removal. Several investigators have demonstrated a stoichiometry between the required coagulant dose and the concentration of humic and fulvic acids in a water sample for turbidity and color removal.[10,12,13,15] This can be explained by a mechanism of adsorption of polymetric cationic aluminum or iron species at the organic surface with concomitant neutralization of the surface charge.[2,11] The uncharged complexes may then flocculate or precipitate, depending on their size, and be removed from solution. Several researchers have obtained results from studies on organics removal by coagulation that are best explained by the precipitation of aluminum of iron humates and fulvates.[10,13]

For the lower-molecular-weight organic compounds, some removal may also occur by processes such as the association of the "neutralized" metal-organic complexes with larger-molecular-weight species during flocculation. The smaller organic compounds may be sufficiently hydrophilic, however, that even if metal ions associate with their functional groups, they are not rendered insoluble and thus removed during coagulation.[16]

Truly dissolved organic compounds may also be partially removed during coagulation[17-20] by complexation, coprecipitation, or adsorption to $Al(OH)_3$ or $Fe(OH)_3$ floc or to incorporated humic and fulvic acid surfaces, but removals of truly dissolved low-molecular-weight compounds are relatively small.

The impact of lime pretreatment on the removal of organics has not been studied extensively in water treatment. Several studies have demonstrated the effectiveness of lime treatment for color removal. Few studies, however, have been conducted to identify the character of organic compounds removed by lime treatment. As discussed previously, color is primarily associated with higher-molecular-weight organic acids; thus the removal of this molecular-weight fraction by lime was expected. However, the increase in TOC in the low-molecular-weight fraction was not anticipated. Molof and Zuckerman[21] reported that the lime treatment of wastewaters caused hydrolysis of high-molecular-weight organics and a shift in the molecular-weight distribution toward lower-molecular-weight compounds. This controversial conclusion was contested in a discussion by Weber,[22] who found no evidence of significant hydrolysis except for the breakdown of proteins. Using a technique of thin-layer chromatography, protein hydrolysis was observed to occur when the sewage was held at pH values above 10 for several hours. This was judged to be a relatively minor effect, however, and "hydrolysis tests" based on altered adsorption characteristics gave no indication of any change in the character of organics in the wastewater.

In this study, the shift in TOC to the <1K fraction was significant. This may have been caused by the hydrolytic breakdown of the organic compounds into smaller fragments, or it may have been caused by the impact of the lime pretreatment on the subsequent rejection efficiency of the ultrafiltration membranes. Ultrafiltration membranes do not exclude all organic molecules with a molecular weight above their stated nominal molecular weight cutoff. Molecular configuration, membrane character, operating pressure, pH, ionic strength, and degree of concentration in the retentate all influence membrane rejection, and some higher-molecular-weight compounds may pass through the membrane while certain lower-molecular-weight molecules may be rejected.

During lime treatment, the concentration of calcium and magnesium ions was reduced, and the ionic strength was decreased relative to the raw water sample and the coagulated samples. The reduced concentration of the divalent cations in solution may have been responsible for the change in the rejection

efficiency of the 1K membrane or the organic content of the water.

It is also possible that the high pH conditions alter the spacial configuration of the fulvic acid molecules in a manner that better affords them passage through the 1K membrane. Even though the solution pH was reduced to a constant level prior to membrane filtration, exposure to high pH values may have caused irreversible changes in organic character that encouraged the movement of a larger fraction of the organics through the 1K membrane.

The results of the fractionation study on the carbon-treated water (pH 7.0) indicate that some high-molecular-weight and some low-molecular-weight organics resisted removal by carbon under the conditions tested. This kind of behavior has been noted previously by several investigators. Although activated carbon absorbs some low-molecular-weight aromatic compounds (e.g., phenolics and pesticides) very well, certain low-molecular-weight compounds typically found in natural waters (e.g., sugar and aliphatic acids) may be very poorly removed.[7,23,24] These latter compounds may be partially degraded in biologically active GAC columns, but in this study, with run times of approximately 1 week, there was little opportunity for significant biological activity to develop. Model compound studies with low-molecular-weight hydrophilic compounds have demonstrated that adsorption capacities for these compounds are very low.[7,24,25] It has also been demonstrated that the adsorption capacity for an organic compound increases as molecular weight increases for compounds in the same homologous series.[25]

Stevens et al[26] employed gas chromatography to evaluate the organic removal effectiveness of activated carbon and noted that larger-molecular-weight, less-volatile organic compounds eluting late during the gas chromatographic analysis were generally better removed than the more volatile early eluters. Chow and David[23] found that when they analyzed the character of organics resistant to adsorption during the treatment of wastewater, the compounds were small (less than 240 nm in dimension), and many were biodegradable. DeWalle and Chian[24] observed that the major fraction of organics removed by activated carbon fell in the molecular-weight range between 100 and 10 000 nmw for studies in which carbon was applied to secondary effluents. Low-molecular-weight material (≤100 nmw) was very poorly removed. The authors noted, however, that there was evidence in their study to indicate that aerobic biodegradation of the low-molecular-weight compounds (≤100 nmw) produced higher-molecular-weight, fulvic-acidlike compounds that were well removed by carbon.

TABLE 9
Molecular weight fractionation study TOC values

Treatment Description	Molecular-Weight Fractionation—*mg TOC/L*				
	≤1K	1-10K	10-100K	≥100K	Total
None	1.47	3.17	0.63	1.07	6.34
Lime	2.07	1.53	0.08	0.23	3.91
Iron-polymer	1.48	1.37	0.00	0.22	3.07
Alum	1.53	1.03	0.00	0.16	2.72
Lime + GAC EBCT = 3.6 min	0.46	0.09	0.02	0.16	0.73
Iron-polymer + GAC EBCT - 2.7 min	0.51	0.00	0.00	0.18	0.69
Alum + GAC EBCT = 2.2 min	0.47	0.02	0.02	0.16	0.69

TABLE 10
Molecular weight fractionation study TTHMFP values

Treatment Description	Molecular-Weight Fraction—*mg TTHMFP/L*				
	≤1K	1-10K	10-100K	≥100K	Total
None	82	225	30	-40	297
Lime	104	84	-5	-29	154
Iron-polymer	95	50	-1	-10	134
Alum	74	59	-1	1	133
Lime + GAC EBCT = 4.5 min	14	12	-8	0	18
Iron-polymer + GAC EBCT = 2.7 min	19	-2	-1	4	20
Alum + GAC EBCT = 2.2 min	19	6	-3	-6	16

Chow and David also found that high-molecular-weight compounds (≤100K nmw) were poorly removed by carbon and explained this observation by invoking "steric difficulty" during their entry into and their subsequent diffusion within the carbon pores. DeWalle and Chian[24] noted that carbon was not effective in removing carbohydratelike compounds with a molecular weight greater than approximately 50K.

Therefore, the carbon removed a broad spectrum of organic compounds but had a low adsorption capacity for the low-molecular-weight hydrophilic organics. The polarity fractionation study indicated that >70 percent of the organic compounds in the carbon column effluents were characterized as hydrophilic compounds (Table 6), and only about 20 percent of the effluent organics were characterized as hydrophobic. The effluent TOC from each of the carbon columns was, therefore, primarily associated with low-molecular-weight hydrophilic compounds.

Measurements of the total trihalomethane formation potential (TTHMFP) in the various molecular weight fractions were conducted for each of the samples tested (Table 10). Some negative values were obtained in this analysis but were a result of the mathematical manipulation of the data rather than experimental considerations. For example, the TTHMFP for the ≥100K fraction of the filtered Mississippi River water is given in Table 10 as −40. This result was obtained because the measured TTHMs in the 100K membrane filtrate exceeded the concentration found in the retentate. But because both numbers were large, the error associated with their difference was significant.

The data obtained were generally consistent, and the summation of the formation potentials in the individual fractions generally came within 10 percent of the distribution of TOC among the different weight fractions, as shown by comparing Tables 9 and 10.

The major contribution to THM production in the filtered river water sample was associated with the 1-10K molecular-weight fraction (225 μg/L); the ≤1K fraction contributed the next largest concentration of THM precursors (82 μg/L). The larger-molecular-weight fractions did not contribute significantly to THM production. Following all the treatments studied, the high-molecular-weight precursors were reduced essentially to zero and the residual precursor concentrations were associated with the low-molecular-weight fractions.

Lime pretreatment caused an apparent increase in the precursor concentration in the ≤1K fraction. In addition, the TOC was also observed to increase in this fraction for lime-treated water. A marginal increase in the ≤1K fraction was also noted for iron-polymer pretreatment, but analysis of the corresponding TOC data in Table 9 indicated that for this pretreatment the TOC in the ≤1K fraction was the same as the river water control. The character of the organics in this weight fraction may have changed, however, because as Tables 5 and 7 indicate, the character of organics in the product differed significantly from the filtered-river-water sample. It is also possible that the particular polymer used in this study may

have contributed to THM formation in the product water. Kaiser and Lawrence[27] found that chlorination of water samples containing commercially available polyelectrolytes produced chloroform. Their studies were conducted with 10 mg Cl_2/L for 4 h, with thermal and ultraviolet excitation used to catalyze THM production. Although their study suggested that the production of chloroform was small, they found a variable response for different polyelectrolytes. The polymer used in this study was not evaluated. Furthermore, the more stringent chlorination conditions (48 mg/L for 48 h) may have caused the formation of higher levels of chloroform than found by Kaiser and Lawrence. Certainly, since there is a lack of information on the chemical composition of commercial polyelectrolyte formulations and their impurities, such as monomers and oligomers, their possible contribution to THM production cannot be overlooked.

Table 10 also shows that lime treatment reduced the precursor concentration in the 1-10K fraction by 63 percent, whereas the coagulation pretreatments provided 74 and 78 percent removal of this fraction. It is apparent, therefore, that low-molecular-weight precursors are poorly removed by the pretreatment processes studied.

Analysis of the precursor concentrations in the carbon-treated waters showed that the concentrations of precursors in the low-molecular-weight fractions were dramatically reduced and that the concentrations in all the column effluents were very similar.

Conclusions

A single sample of Mississippi River water was subjected to various pretreatments (lime softening, alum coagulation, and iron-polymer coagulation) before being applied to columns of granular activated carbon. Samples of water were taken from the raw river water, after pretreatment, and after carbon adsorption. The organic content of these samples was characterized, and the following conclusions can be drawn from analysis of the data collected.

- Forty percent of the organic content of the sample was characterized hydrophobic and 60 percent hydrophilic.
- The molecular-weight distributions of the river water for the fractions ≤1K, 1-10K, 10-100K, and ≥100K were 23, 50, 10, and 17 percent, respectively, based on TOC analyses.
- Pretreatment with alum, iron-polymer, or lime resulted in the removal of mainly acidic and neutral organic compounds. Hydrophobic organics were slightly better removed than hydrophilic compounds. Coagulation gave better organics removal, but lime addition was not optimized for organics removal.
- Total trihalomethane formation potential analyses were conducted on polarity fractions for the differently treated waters. Trihalomethane precursors were almost evenly split between the hydrophobic and hydrophilic fractions in the raw water. However, the hydrophobic precursors were more effectively removed during pretreatment.
- There appeared to be significant differences in the character and distribution of THM precursors between lime-treated and coagulated waters before and after GAC treatment.
- Higher-molecular-weight organics were most effectively removed during pretreatment; lower-molecular-weight organics were effectively reduced by GAC.
- After lime treatment, the concentration of low-molecular-weight organics (≤1K) appeared to increase (by approximately 30 percent); coagulation had no significant impact on this fraction.
- The effluent samples from GAC contained mainly low-molecular-weight hydrophilic neutral and acidic organics.

Acknowledgment

The authors thank the USEPA for financial support via grant CR806377.

References

1. Semmens, M.J. et al. Optimizing Coagulation-Adsorption for Haloform and TOC Reduction. USEPA Final Rept., Grant CR806377 (1982).
2. Committee Report. Organics Removal by Coagulation: A Review and Research Needs. *Jour. AWWA*, 72:10:588 (1980).
3. Staples, A. Characterization of Naturally Occurring Organics in Untreated, Pretreated, and Activated Carbon Treated River Water. Master's thesis, Univ. of Minnesota, Minneapolis (June 1982).
4. Semmens, M.J. & Field, T.K. Coagulation—Experiences in Organics Removal. *Jour. AWWA*, 72:8:476 (Aug. 1980).
5. Leenheer, J.A. & Huffman, E.W.D. Classification of Organic Solutes in Water Using Macroreticular Resins. *USGS Research Jour.*, 4:6:737 (1976).
6. Leenheer, J. Comprehensive Approach to Preparative Isolation and Fractionation of Dissolved Organic Carbon From Natural Waters and Wastewaters. *Envir. Sci. & Technol.*, 15:5:478 (1981).
7. Mullins, R.L. et al. The Effectiveness of Several Brands of Granular Activated Carbon for the Removal of Trihalomethanes From Water. *Proc. Activated Carbon Sym.* Miami, Sept. 10-15, 1978.
8. Eisenreich, S.J. et al. Metal Transport Phases in the Upper Mississippi River. *Particulates in Water*. ACS, Washington, D.C. (1980).
9. Gjessing, E.T. & Lee, G.F. Fractionation of Organic Matter in Natural Water in Sephadex Columns. *Envir. Sci. & Technol.*, 1:631 (1967).
10. Black, A.P. et al. Stoichiometry of Coagulation of Color-Causing Organic Compounds With Ferric Sulfate. *Jour. AWWA*, 55:10:1347 (Oct. 1963).
11. Bowie, J.E. Jr. A Comparison of Aluminum Sulfate and Activated Carbon for Organic Color Removal From Groundwaters. Master's thesis, Mississippi State Univ. (1975).
12. Black, A.P. & Willems, D.K.G. Electrophoretic Studies of Coagulation for Removal of Organic Color. *Jour. AWWA*, 53:4:438 (Apr. 1961).
13. Hall, E.S. & Packham, R.F. Coagulation of Organic Color With Hydrolyzing Coagulants. *Jour. AWWA*, 57:9:7149 (1965).
14. Shaw, D.J. *Introduction to Colloid and Surface Chemistry*. Butterworth Publishers, Boston (1970).
15. Edzwald, J.K. Coagulation of Humic Substances. *Proc. AIChE Sym.*, Atlanta, Ga., 1979.
16. Semmens, M.J. & Ayers, K. Removal by Coagulation of Trace Organics From Mississippi River Water. *Jour. AWWA*, 77:5:79 (May 1985).
17. Ayers, K. Removal of Organic Material From Mississippi River Water by Coagulation with Alum and Ferric Sulfate. Master's thesis, Univ. of Minnesota (1980).
18. Chapman, G. & Rae, A.C. *Nature*, 214:627 (1967).
19. Semmens, M.J. & Ocanas-Sanchez, G. Removal of Specific Trace Organics From Water During Chemical Coagulation. *AIChE Sym. Series 1677*, 73:42 (1976).
20. Sridharan, N. & Lee, G.F. *Envir. Sci. & Technol.*, 6:12:1031 (1972).
21. Zuckerman, M.M. & Molof, A.H. High Quality Reuse Water by Chemical Physical Wastewater Treatment. *Jour. WPCF*, 42:3:437 (1970).
22. Weber, W. Discussion of High Quality Reuse Water by Chemical Physical Wastewater Treatment. *Jour. WPCF*, 42:3:437 (1970).
23. Chow, K. & David, M.M. Compounds Resistant to Carbon Adsorption in Municipal Waste Treatment. *Jour. AWWA*, 69:4:555 (Apr. 1977).
24. DeWalle, F.B. & Chian, E.S.K. Removal of Organic Matter by Activated Carbon Columns. *Jour. ASCE*, 100:189 (1974).
25. Weber, W.J. *Physicochemical Processes for Water Quality Control*. Wiley Interscience, New York (1972).
26. Stevens, A.A. et al. Removal of Higher Molecular Weight Organic Compounds by the Granular Activated Carbon Adsorption Unit Process. *Proc. Practical Application of Adsorption Techniques in Drinking Water*. Reston, Va., 1979.
27. Kaiser, K.L. & Lawrence, J. Polyelectrolytes—Potential Chloroform Precursors. *Science*, 196:1205 (June 1977).

About the authors: *Since 1977 M.J. Semmens has been associate professor of environmental engineering, Department of Civil and Mineral Engineering, University of Minnesota, 122 Civil and Mineral Engineering Bldg., 500 Pillsbury Dr. S.E., Minneapolis, MN 55455-0220. A graduate of Imperial College of Science and Technology, London (BS); of Harvard University, Cambridge, Mass. (MS); and of University College, London (PhD), Semmens's research activities have focused on physical-chemical processes, including ion exchange, adsorption, and coagulation. A.B. Staples is a senior environmental engineer in the Environmental Engineering Section, 3M Co., St. Paul, MN 55144.*

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.